

## ADVANCES IN DIRECT METHANOL FUEL CELLS at, JPL

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### ABSTRACT

A new liquid feed direct methanol fuel cell has been developed based on a proton exchange membrane electrolyte and Pt/Ru and Pt catalyzed carbon fuel and air/O<sub>2</sub> electrodes respectively. The cell has been shown to deliver significant power outputs at moderately low temperatures of 25 to 60 °C. At 60 °C, output is near 100 mA/cm<sup>2</sup> at a potential greater than 0.5 V. A deterrent to performance appears to be methanol crossover through the membrane to the oxygen electrode. Further improvements in performance appear possible by minimizing the methanol crossover rate.

### 1. INTRODUCTION

Under a task sponsored by the Defense Research Projects Agency (DARPA), JPL is engaged in development of direct methanol fuel cells (DMFC). This effort is being carried out in conjunction with other organization of a DARPA Fuel Cell Team that includes universities as well as government labs and industrial organizations. A near term JPL objective is to develop and demonstrate a laboratory type DMFC employing advanced materials (catalysts and electrolytes) being developed by the universities and other organizations.

Two types of DMFC's have been examined in the past. One employs a liquid acid electrolyte, introduces the methanol as a liquid, and typically operates near 60 °C. The other employs a solid polymeric type electrolyte, introduces the methanol as a gas or vapor, and typically operates near 90 °C. Problem areas with the liquid electrolyte type are as follows: a) requires expensive materials of construction to withstand corrosion problems associated with the use of acids, b) safety issues associated with the use of these acids, and c) parasitic shunt currents with multi-cell stacks of these. Problems associated with the solid electrolyte gas feed type are as follows: a) requires good humidity control to maintain functionality of the solid electrolyte and b) requires a great deal of accessory equipment to maintain the humidity as well as to feed and vaporize the MeOH into the cell. The CO<sub>2</sub> end product from the

reaction is readily separable from the liquid MeOH discharge end products in the case of the liquid electrolyte cell, but not from the MeOH vapor end products in the case of the solid electrolyte cell. The ease of separation is an advantage for the liquid electrolyte cell in that it enables easy recovery of pure MeOH in the effluent for recycling back to the cell inlet (an important consideration from a systems point of view).

Initially JPL began development of both types of cells for the pl anneal electrolyte and catalyst studies. The liquid electrolyte cell was found to be functional but to deliver only about 30 to 50 mA/cm<sup>2</sup> at potentials of 0.3 to 0.4V, as described in the literature. Some difficulty was encountered at the start in maintaining a proper water balance in the case of the gas feed solid electrolyte type of cell. When balance was obtained, for short periods of time, the output was, however, found to be low and comparable to the above.

Subsequent efforts yielded very discouraging results with the gas feed cell but encouraging results with the liquid feed cell. In the case of the gas feed cell the problem of moisture balance continued to be a problem and impact performance to such a degree, that after only about one hour of operation, this factor dominated performance. Numerous attempts were made to control the moisture, but these were all unsuccessful. In contrast to this the moisture balance of the liquid feed cell was quite manageable and findings were made of important new modifications that could markedly improve performance of this type of cell. These findings involved: 1) use of additives to enable the use of existing gas diffusion electrodes in the liquid cell, 2) use of the polymer electrolyte in the liquid feed design, and 3) that there is no need for the acid addition to the electrolyte. Results showed that outputs of 100 mA/cm<sup>2</sup> at 0.3 to 0.4 V were readily achievable and the liquid feed cell can indeed deliver significant outputs at very moderate temperatures.

On this basis JPL focused its primary effort on the liquid feed system and has continued optimization studies to raise output to even higher levels with advanced materials and cell designs,

This paper reviews highlights of progress to date on development of the liquid feed MeOH system.

## 2. DESCRIPTION OF CELLS

### 2.1 Liquid Feed Cell and Reactions

A schematic diagram of the liquid feed cell along with overall cell reactions is given in Figure 1. The cathode or air/O<sub>2</sub> electrode consists of a catalyzed layer of carbon one side of which is exposed to air or O<sub>2</sub> and the other side of which is in contact with the electrolyte layer. The anode or, fuel/MeOH electrode, consists

of another catalyzed layer of carbon one side of which is exposed to MeOH solution and the other side of which is in contact with the electrolyte. The electrolyte is a solid layer of proton exchange membrane. Air or  $O_2$  is continuously swept through the cathode compartment and MeOH solution is continuously swept through the anode compartment as shown in this figure.  $H_2SO_4$  was added to the MeOH solution initially but this was subsequently found unnecessary. Also shown in this figure are the individual elect-rode reactions as well as the overall cell reaction.

## 2.2 Half Cell For Initial MeOH Oxidation Studies

Initial methanol oxidation studies were carried out with the half cell assembly as shown in Figure 2. The test electrode, typically a catalyzed carbon coupon, is immersed in the liquid fuel and driven against a counter electrode which was a platinum sheet. Potential of the test electrode was measured against a  $Hg/Hg_2SO_4$  reference electrode positioned adjacent to the test electrode.

## 2.3 Advanced Cell With Membrane Electrolyte

Figure 3 gives a schematic diagram of the complete laboratory type liquid feed MeOH system employing the membrane electrolyte. The liquid feed cell for this system is actually a modified version of a gas feed cell. Major components consist of a membrane-electrode assembly (MEA) and the cell hardware. The MEA consists of a layer of Nafion electrolyte, 7 mil thick, with fuel and air/ $O_2$  electrodes bonded to either side. Electrode dimensions are 2 inch by 2 inch by approximately 10 mil thick. The MEA is positioned between the machined portion of two graphite blocks. The machined area on each on each block is a rectangular pattern with open channels (designated as flow field) to allow flow of liquid or gas across the electrode surface. Inlet and outlet ports communicate with the flow fields via holes drilled into the carbon blocks and equipped with threaded fittings at the sides of the blocks. Stainless steel support plates, with the same overall length and width as the carbon plates, are located on the back surface of the plates. The stainless steel plates, as well as the carbon blocks, are drilled in their outer perimeter to accommodate bolts that are used to compress the assembly for sealing and to provide electrical contact between the electrode and the un-recessed area of the flow field.

The MeOH solution is introduced into the fuel compartment of the cell via a pump and then returned to a fuel storage reservoir as shown in Figure 3. The end product, carbon dioxide, is entrapped in the exit fuel line and released in the storage reservoir. pressurized air or  $O_2$  is introduced to the air compartment of the cell and vented without circulation. Heaters are located on the outside surface of the cell to control cell temperature. Finally, the cell is equipped with a small closed end hole to accommodate an internal thermocouple and an open ended hole to accommodate a reference electrode. The latter reference enabled measurement of

individual fuel and  $O_2$  electrode polarizations.

### 3. RESULTS AND DISCUSSION

#### 3.1 Initial Findings: Use of Gas Diffusion Electrodes and Pt/Ru Catalysts

An important initial finding was that existing gas diffusion electrodes, such as employed in  $H_3PO_4$  Cells, can be made to function well in the liquid feed environment, containing  $H_2SO_4$  electrolyte, by addition of a small amount of additive to the electrolyte. Next, it was found that MeOH is oxidized more readily (less polarization) with a bimetallic catalyst of Pt and Ru than with a Pt catalyst alone.

#### 3.2 MeOH Oxidation Studies

Employing these two findings, a series of runs was carried out in the half cell to determine sensitivity of MeOH oxidation to design and operational parameters and results are given in Figures 4, 5, and 6. Figure 4 reveals that MeOH oxidation is improved with increase in temperature. For example, as temperature is raised from 25 to 60 °C, the fuel electrode polarization at 100 mA/cm<sup>2</sup> is reduced by almost 200 mV. Figure 5 reveals that MeOH oxidation is improved by increase in fuel concentration. For example as MeOH concentration is raised from 1M to 8M, the fuel electrode polarization is reduced by more than 200 mV. Finally, Figure 6 shows that MeOH oxidation is improved by an increase in catalyst loading. For example, as loading is increased from 0.5 to 5 mg Pt/Ru/cm<sup>2</sup>, the polarization near 80 mA/cm<sup>2</sup> is reduced by over 400 mV.

#### 3.3 Elimination of $H_2SO_4$

Another finding was that the addition of  $H_2SO_4$  to the MeOH solution was unnecessary when the electrodes are incorporated into the MEA. This finding was deemed important in that the elimination of  $H_2SO_4$  would alleviate the threat of intercell shunt currents in follow on multi-cell designs that were contemplated to require a bipolar electrode configuration.

#### 3.4 Performance of Advanced Cell With Membrane Electrolyte

Figure 7 gives the F/I performance characteristics of the advanced cell as a function of MeOH concentration of the fuel at 140 to 160 °F, and with pure  $O_2$  as oxidant and Pt/Ru and Pt as fuel and  $O_2$  electrode catalysts respectively at loadings of 0.5 mg/cm<sup>2</sup>. The results reveal a trend of increased output (voltage) as concentration is increased beyond 0.5M and a reduction in output (voltage) as concentration is increased higher than 2M.

Apparently the output exhibits a maximum with increasing fuel concentration from 0.5 to 4M. The maximum output for this series with 2M was, for example, near 0.53V at 3.00 mA/cm<sup>2</sup>. This output is reasonably high and approaching the range of interest for practical applications

The increase in output, as concentration is increased higher than .514, is attributed to the trend of increased output of the fuel electrode with MeOH concentration as noted above. The decrease in output with concentration from 2M to 4M is contrary to this trend and must therefore be due to other factors. Based on the known permeability of MeOH in the membrane, it was speculated that this other factor may be due to fuel "crossover" to the O<sub>2</sub> electrode wherein the fuel reacts with and lowers the potential of this electrode.

In order to examine this phenomena in greater detail, a series of runs was carried out- in which the O<sub>2</sub> electrode potential was measured with various fuel concentrations. Results are shown in Figure 8. Therein it was found that the potential of the O<sub>2</sub> electrode was markedly reduced as fuel concentration was increased from 2 to 4M MeOH. For example, the O<sub>2</sub> electrode potential was noted to drop more than 100 mV at 100 mA/cm<sup>2</sup> as MeOH concentration was increased from 2 to 4 m MeOH. This finding confirms that the reduction in output with concentration at the higher concentration levels is indeed due to a marked decrease in the potential of the O<sub>2</sub> electrode. The finding also tends to support the belief that this reduction is due to MeOH crossover in that the crossover rate increases with fuel concentration. Furthermore, this finding emphasizes the need to minimize the crossover rate to improve performance of the O<sub>2</sub> electrode, and hence the overall cell performance.

This work is continuing with emphasis on examination of methods to minimize the crossover phenomena and other factors to improve overall cell performance.

Finally, it is well to point out. that the cell output appears to be quite stable. Except for the very highest outputs beyond about 200 mA/cm<sup>2</sup>, the indicated voltages on the E/I curves remain essentially constant (within about 5mV) for well over 1 hr of continuous operation. At the lower currents less than 100 mA/cm<sup>2</sup>, the outputs have been shown to hold constant (again within 5mV) for over 8 hours of continuous operation.

#### CONCLUSIONS

- 1) A new liquid feed DMFC has been developed based on a proton electron transfer membrane electrolyte, Pt/Ru catalyzed fuel electrode and Pt catalyzed air/O<sub>2</sub> electrodes.
- 2) The new liquid feed DMFC can deliver significant outputs in excess of 100 mA/cm<sup>2</sup> at potentials greater than 0.5 V at moderate

temperatures of 60 °C.

3) Pt/Ru catalyzed carbon electrodes are well suited for oxidation of MeOH.

4) Performance of Pt/Ru catalyzed carbon electrodes increases with increased temperatures (25 to 60 °C), increased fuel concentration (0.5 to 2 M MeOH), and increased catalyst loading (0.5 to 5 mg/cm<sup>2</sup>).

5) Performance of the new liquid feed fuel cell should improve with reduction in the amount of fuel crossover.

#### ACKNOWLEDGEMENT

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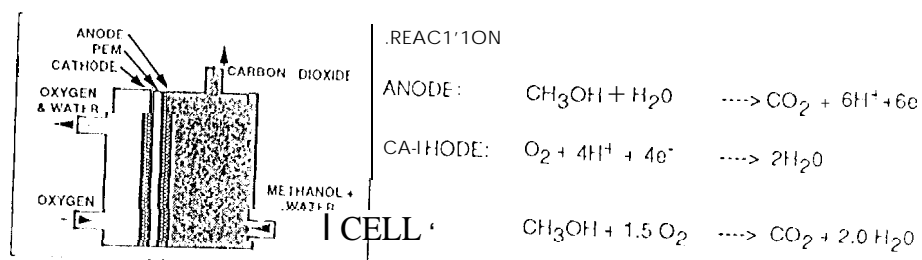


Figure 1 Schematic Diagram of Liquid Feed Direct Methanol Fuel Cell and Cell Chemistry

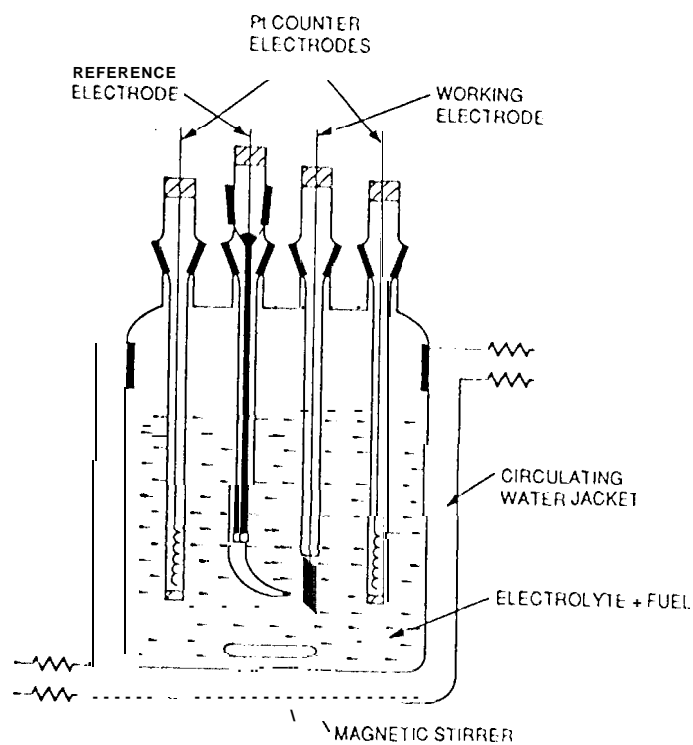


Figure 2 Schematic Diagram of an Experimental Liquid Feed Half Cell

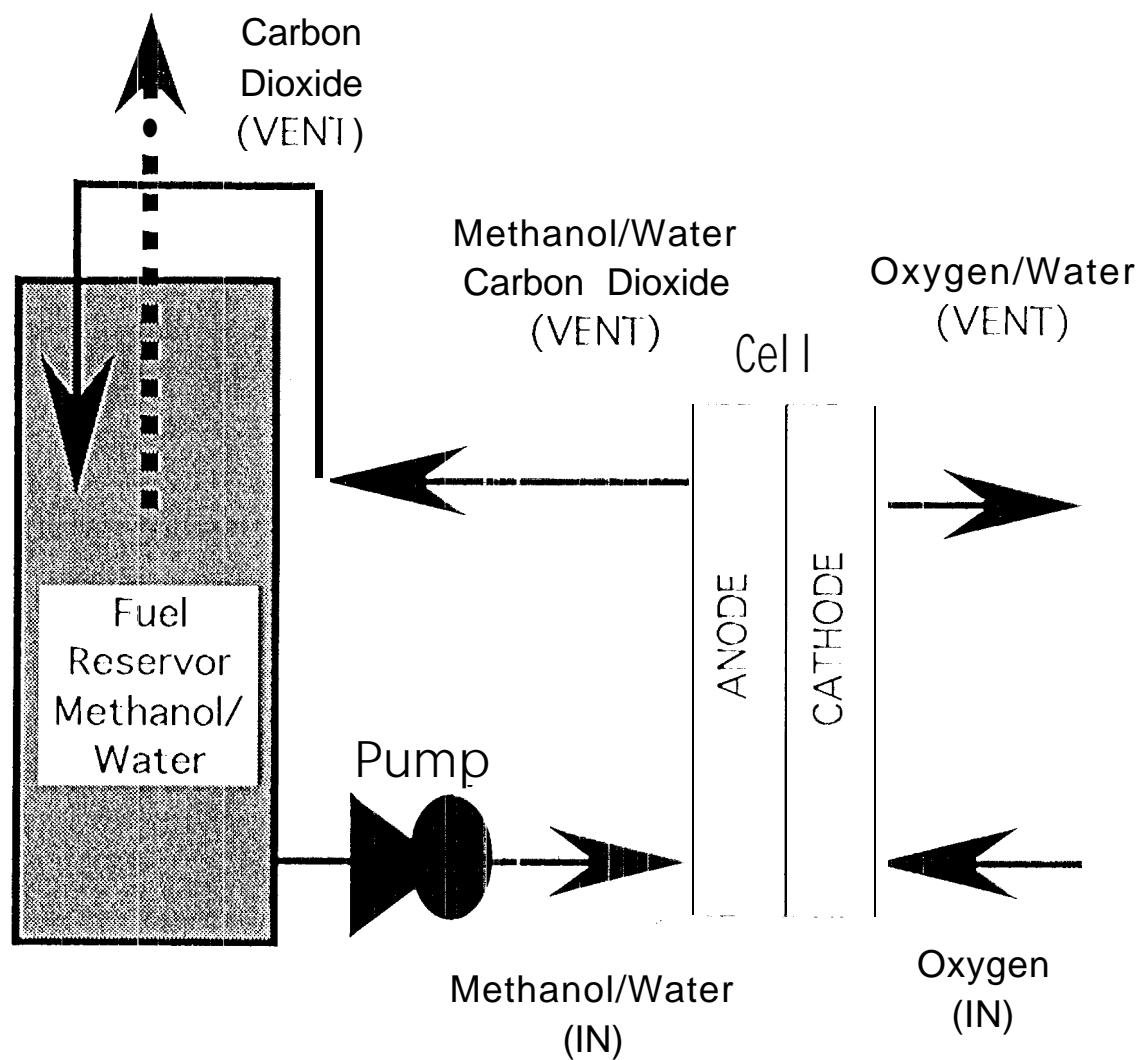


Figure 3 Schematic Diagram of Complete 1 Laboratory Type 1 Liquid Feed MeOH System



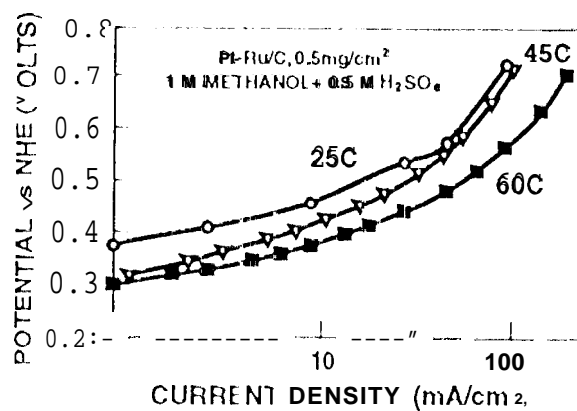


FIGURE 4 Effect of Temperature on Methanol Oxidation

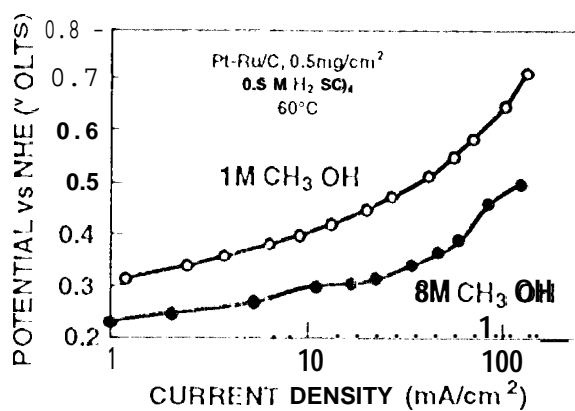


FIGURE 5 Effect of Concentration on Methanol oxidation

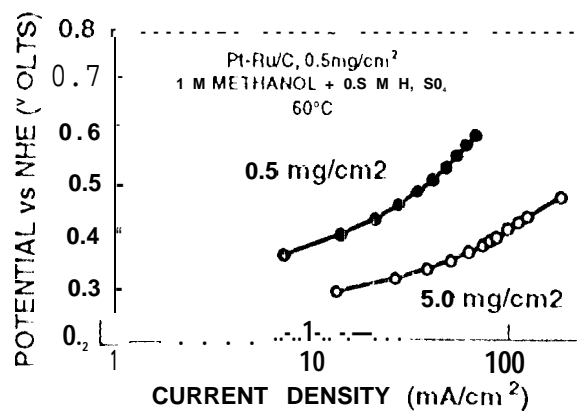


FIGURE 6 Effect of Catalyst Loading on Methanol oxidation

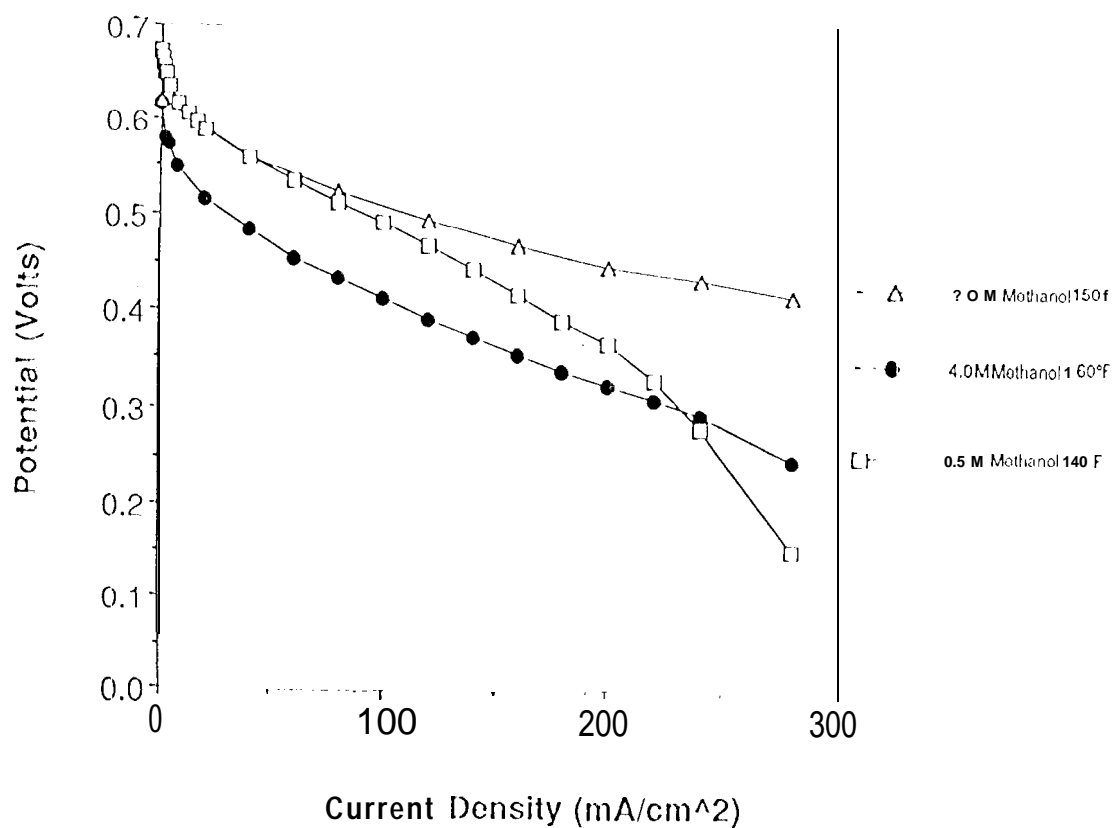


Figure 7 Effect of Methanol Concentration on Performance of Advanced Laboratory Cell with Membrane Electrolyte

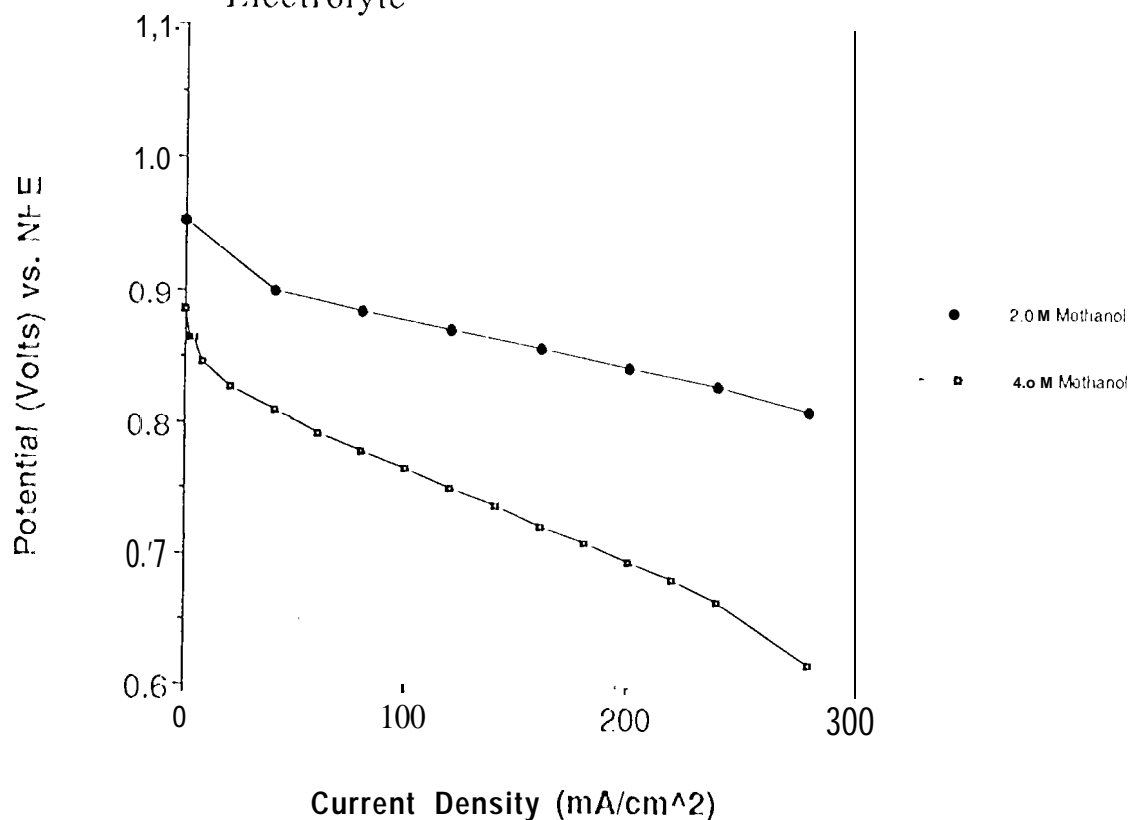


Figure 8 Effect of Methanol Concentration on Performance of Oxygen Electrode of Advanced laboratory Cell with Membrane Electrolyte